Report on the 1988 Workshop on Supercritical Fluid Chromatography

The success of this first Workshop on Supercritical Fluid Chromatography (SFC) held in Park City, Utah, January 12-14, 1988 was a tribute to the efforts of its coorganizers, Professors Milton Lee and Karin Markides of Brigham Young University. The workshop attracted over 160 attendees to a program consisting of 39 formal presentations supplemented by nine discussion sessions. The program brought together a virtual "who's who" in the field of analytical supercritical fluid technology and was enriched by the many informal discussions held by the speakers and participants. A particularly useful addition to the oral program was the issuance of a compendium of 335 chromatograms, which covered twelve generic categories of compounds separated by SFC. Formal discussion sessions covered such topics as mobile phases, injection techniques, supercritical fluid extraction coupled with chromatography, detectors, and column technology.

A seminal theme throughout the workshop consisted of advances in detector methodology, a vexing area of SFC that has progressed considerably from the days when visual detection of porphyrin moieties was accomplished with the aid of a sight glass (M. L. Lee). Current usage of the various detection modes was summarized by H. H. Hill (Washington State) in a formal discussion session. The preponderance of analyses are accomplished with flame ionization and ultraviolet detectors followed by mass spectrometers and infrared detectors. Despite the above trend, a number of novel approaches were cited during the workshop and documented in the applications manual. Noteworthy were the use of ion mobility detection for the analysis of pesticides and antibiotics and K. Grolimund's (Ciba-Geigy-Basel) incorporation of chemiluminescence to selectively determine nitrosamines. D. J. Bornhop (Lee Scientific) described the characteristics and problems of constructing a capillary-compatible UV detector. Here, as in many detector designs, there is a tradeoff between postcolumn solute dispersion and detection levels.

Seven formal presentations were devoted to advances in SFC/mass spectrometry. J. D. Henion (Cornell) enumerated the fundamental aspects of coupling a supercritical fluid chromatograph with a mass spectrometer, while J. D. Pinkston related Procter & Gamble's experience in evaluating various mass spectrometers in tandem with SFC. Interesting applications of the above combination were noted by A. J. Berry (Cardiff) and the Glaxo research group for monitoring fermentation broth constituents and a host of pharmaceutical compounds. The experience of the Brigham Young University research team with high resolution mass spectrometry coupled with SFC was recounted by E. C. Huang (Brigham Young University) for a variety of drugs and pesticides. A detection limit of 20 pico-grams was quoted for heptachlor at a signal-to-noise level of 3. The discussion session which followed was initiated by B. W. Wright's (Battelle) comments on the sensitivity levels to be expected in both the electron impact and chemical ionization modes of mass spectrometry under full scan and "best" detection limits.

Many novel approaches were presented for achieving separations by SFC. An early discussion by R. D. Smith (Battelle) highlighted the use of reverse micelle mobile phases for solubilizing solutes in supercritical fluid phases. It is apparent that such an approach offers some intriguing possibilities to the separation scientist; however, much more research will be required to demonstrate its general analytical utility. Controversy surrounded the concept of negative temperature programming during the workshop program, but data presented in both the initial lecture by E. G. Klesper (Aachen) and the final presentation by D. Ishii (Nogoya University) demonstrated the potential of the technique, particularly with respect to oligomer separations. An unusual liquid crystal stationary phase was also introduced during the meeting by H.-C. K. Chang (Brigham Young University). The recorded retention trends for polynuclear aromatic hydrocarbons on this bonded phase were found to be similar to those recorded in gas chromatography; that is, retention was dependent on the length-to-breadth ratio of the solute molecule. Other useful separations, such as the resolution of estrogens and cis/trans fatty acids, were demonstrated with this capillary column. The use of sample derivatization as a means of enhancing solute volatility and detectability in SFC was advocated by several of the participants. V. N. Reinhold (Harvard), borrowing on previous work reported by T. L. Chester (Procter & Gamble), used permethylated derivatives to perform chromatography on glycolipids, gangliosides, and maltodextrins. Similar applications were demonstrated by M. Novotny (Indiana University) for a variety of biomolecules. Novotny also discussed the use of derivatizing agents for introducing specific elements into a compound to enhance its detectability by element-sensitive detectors.

A session devoted to coupling supercritical fluid extraction in-line with SFC promoted considerable discussion. Lectures by H. Engelhardt (Universitat des Saarlandes) and S. B. Hawthorne (University of North Dakota) demonstrated the usefulness of the technique to an array of solute/sample matrix combinations. In the method presented by Engelhardt, relatively large quantities of carbon dioxide are used to completely remove the desired solutes from the sample contained in a small micro chamber. The extracted sample is then transferred through a valve to the head of a packed column for SFC. A similar principle is also employed in the method described by Hawthorne, but even smaller extraction cells are utilized and the sample is introduced directly onto the head of a conventional capillary GC column. The use of such small sampling cells raises the question of whether a truly representative sample is being extracted, however the technique may have merit in cases where physical size of the sample is limited. Additional applications of this coupled technology were mentioned later in the workshop and it promises to be an area

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of future growth with the availability of commercial instrumentation.

The diversity and number of SFC applications presented during the workshop are too voluminous to detail in this short review. However, several examples may serve to illustrate the broad spectrum of applications to which SFC has been applied. An excellent lecture by P. Sandra of the Research Institute for Chromatography in Belgium critically assessed the role of SFC in the analysis of lipids. Particularly noteworthy was the use of derivatization for the analysis of phospholipids, a class of solutes which do not possess adequate solubility in neat supercritical carbon dioxide. Excellent examples of triglyceride, fatty acid, and associated oleochemical separations were also presented by Y. Hirata (Toyohashi University) on packed columns and by T. Greibrokk (University of Oslo) for capillary SFC. The use of SFC for the determination of polymer additives was well demonstrated in the applications book. However, the presentation by K. D. Bartle (University of Leeds) was particularly impressive, with over twenty-one common additives being separated during one chromatographic analysis. Detection in this study was accomplished by both flame ionization and Fourier transform infrared spectrometry.

The current state of the art in petroleum SFC separations was stated in a lecture by J. M. Levy (BP America). Levy illustrated the power of SFC in this field with numerous chromatographic separations attained by both capillary and packed column methods, multidimensional approaches, and extraction coupled with chromatography. The use of SFC for simulated distillation experiments was also noted by Levy and an impromptu session on this topic was an addendum to the formal workshop. SFC is a very powerful technique for examining industrial products composed of lipophilic materials, since these mixtures can be readily separated by pressure programming the mobile phase. S. G. Yocklovich (Computer Chemical Systems) demonstrated this concept on the oil and wax components contained in an emulsion agent for treating fibrous products. Deformulation experiments with SFC were also presented by J. W. King (USDA) for complex pharmaceutical products. A particularly elegant study was reported by D. W. Later (Lee Scientific) in which SFC was utilized for the analysis of pesticide metabolites in biological matrices. The study consisted of monitoring the appearance of the principal metabolites of aldicarb or carbaryl by means of FID and NPD detectors. The results from this study showed excellent agreement with the data obtained by HPLC and liquid scintillation methods. Extraction of the aldicarb from freeze-dried cells was effected by supercritical carbon dioxide in a micro extraction cell.

An excellent overview of the workshop was presented by Professor Milos Novotny after a final spirited discussion session. In the author's opinion, the success of this workshop can be largely attributed to its unique format which permitted intensive informal discussions along with the formal presentation schedule. Current plans call for a repeat of this workshop within one to two years. It should be well attended given the success of the inaugural workshop and the torrid research pace in SFC.

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